FLOWCAMP

REDOX FLOW BATTERY CAMPUS

MARIE SKŁODOWSKA-CURIE EUROPEAN TRAINING NETWORK "FLOWCAMP" (H2020-MSCA-ITN-2017) TO IMPROVE MATERIALS FOR NEXT-GENERATION REDOX-FLOW BATTERIES

An Enhanced 1D Model of a Hydrogen-Bromine Flow Battery

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H_2/Br_2 FLOW BATTERY

Many renewable energy sources are currently in operation across the World, such as wind turbines and solar panels, however they often rely on natural phenomena to generate power which is not reliable at all times. Energy storage systems are required to enable renewable energy to become competitive and reduce green house gas emissions.

Hydrogen bromine flow batteries (HBFB) utilise a hydrogen oxidation/evolution and bromine/bromide redox reactions. During discharge, hydrogen gas forms protons, which travel across a proton-exchange membrane. At the same time, dissolved in water bromine reacts in the porous electrode to form bromide ions. This technology promise long lifetime (20 years), low levelized cost of storage, and high power densities. However, it is currently hindered by bromide crossover shortening battery life.

MOTIVATION

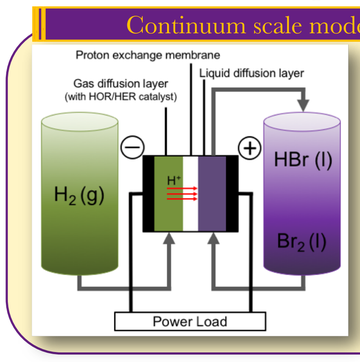
Implementation of computer modelling will accelerate the battery development process and optimization. Modelling and simulation in conjunction with experimental validation will prove beneficial for analysing the effect of cell design on performance.

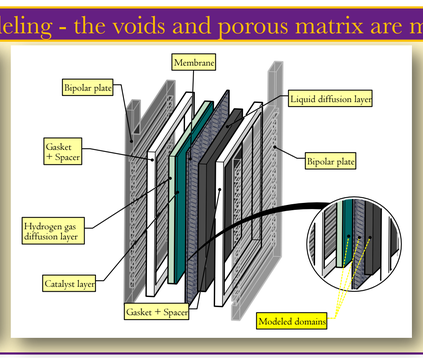
In order to achieve promising modelling results of dynamic processes (transport phenomena, electrode kinetics), a firm understanding of static processes (thermodynamics, from which the driving potentials stem), is necessary. Upon a revival of the water-bromine-bromide system as a potential candidate to be utilized in redox flow batteries and more advanced measurement techniques available nowadays, further research is needed to describe its key characteristics. The currently existing data on polybromide equilibria gives only apparent equilibrium constants. A search for a method yielding true, thermodynamic constants is highly desired in order to describe this flow battery system with better accuracy.

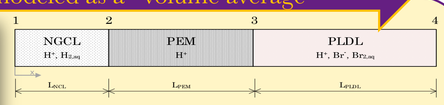
1D MACROHOMOGENEOUS MODEL

$$H_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,H^+ + 2\,e^- \qquad Br_2 + 2\,e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,Br^-$$

Continuum scale modeling - the voids and porous matrix are modeled as a "volume average"







- ✓ 1D through-plane transport of species (diffusion only) and charge
- ✓ Isothermal, isobaric
- ✓ Porous electrode theory
- ✓ Effective transport properties (D, σ)

Governing equations

Fluxes and conservation law

$$\vec{N}_i = -\left[D_i \nabla c_i - c_i \vec{v} + u_i F z_i c_i \nabla \phi_l\right]$$
$$\vec{j}_s = -\sigma_s \nabla \phi_s$$
$$\vec{j}_l = F \sum_i z_i \vec{N}_i \qquad D_i^{\text{eff}} = \varepsilon^{1.5} D_i$$
$$\nabla \cdot \vec{\Gamma} = S \qquad \sigma_l^{\text{eff}} = \varepsilon^{1.5} \sigma_l$$

Surface concentration estimations

$$\frac{D_{\text{Br}^-}}{r_p}\left(c_{\text{Br}^-} - c^s_{\text{Br}^-}\right) = \frac{j_+}{F}$$
$$\frac{D_{\text{Br}_2}}{r_p}\left(c_{\text{Br}_2} - c^s_{\text{Br}_2}\right) = -\frac{j_+}{2F}$$

Electrochemistry of the Br_2 side (incl. mass transport & concentration dependence)

$$\eta_- = \phi_s - \phi_l - E_{\text{eq},-} \qquad \delta_{\text{EDL}} = \sqrt{\frac{\epsilon_w \epsilon_0 k_B T}{2 c^*_{\text{H}^+} N_A z^2_{\text{H}^+} e^2_{\text{elm}}}}$$
$$\eta_+ = \phi_s - \phi_l - E^*_{\text{eq},+}$$
$$E_{\text{eq},+} = E^\circ_+ + \frac{RT}{2F} \ln\left(\frac{c^s_{\text{Br}_2}/c^\circ}{(c^s_{\text{Br}^-}/c^\circ)^2}\right)$$
$$j_+ = j_{0ref,+}\left[\left(\frac{c^s_{\text{Br}^-}}{c^*_{\text{Br}^-}}\right)^{p_{\text{Br}^-}}\left(\frac{c^s_{\text{Br}_2}}{c^*_{\text{Br}_2}}\right)^{p_{\text{Br}_2}} \exp\left(\frac{\alpha_{a,+}F}{RT}\eta_+\right) - \left(\frac{c^s_{\text{Br}^-}}{c^*_{\text{Br}^-}}\right)^{q_{\text{Br}^-}}\left(\frac{c^s_{\text{Br}_2}}{c^*_{\text{Br}_2}}\right)^{q_{\text{Br}_2}} \exp\left(-\frac{\alpha_{c,+}F}{RT}\eta_+\right)\right].$$
$$p_i = \begin{cases} 2 & \text{for } i = \text{Br}^- \\ 0 & \text{for } i = \text{Br}_2 \end{cases} \qquad q_i = \begin{cases} 0 & \text{for } i = \text{Br}^- \\ 1 & \text{for } i = \text{Br}_2 \end{cases}$$
$$j_{0,+} = j_{0\text{ref},+}\left(\frac{c^s_{\text{Br}^-}}{c^*_{\text{Br}^-}}\right)^{\gamma_{\text{Br}^-}}\left(\frac{c^s_{\text{Br}_2}}{c^*_{\text{Br}_2}}\right)^{\gamma_{\text{Br}_2}}$$

Dependent variables solved for:

Notation	Units	Description
ϕ_s	V	Electrostatic potential (in the solid phase)
ϕ_l	V	Ionic potential (in the liquid phase)
$c_{\text{Br}_2,\text{aq}}$	mol m^{-3}	Concentration of dissolved bromine gas
$c_{\text{H}_2,\text{aq}}$	mol m^{-3}	Concentration of dissolved hydrogen gas
c_{Br^-}	mol m^{-3}	Concentration of bromide anions
c_{H^+}	mol m^{-3}	Concentration of protons

Accounting for:

- ✓ Donnan potential
- ✓ Hydrogen gas absorption
- ✓ Porosity of carbon electrode
- ✓ Nernstian losses
- ✓ Limiting current density
- ✓ Influence of concentration on electrochemical constants

OPEN-CIRCUIT POTENTIAL VS STATE OF CHARGE

The water-bromine-bromide system thermodynamics

Possible reactions [1]

$$1/2\ Br_2 + e^- \rightleftharpoons Br^-$$
$$3/2\ Br_2 + e^- \rightleftharpoons {Br_3}^-$$
$$5/2\ Br_2 + e^- \rightleftharpoons {Br_5}^-$$
$$1/2\ {Br_3}^- + e^- \rightleftharpoons 3/2\ Br^-$$
$$1/4\ {Br_5}^- + e^- \rightleftharpoons 5/4\ Br^-$$
$$3/2\ {Br_5}^- + e^- \rightleftharpoons 5/2\ {Br_3}^-$$

Reduction to independent reactions

$$Br_2 + Br^- \overset{K_3}{\rightleftharpoons} {Br_3}^- \qquad K'_3 = \frac{[c_{Br_3^-}]/c^\circ}{[c_{Br_2}][c_{Br^-}]/c^{\circ 2}}$$
$$2\,Br_2 + Br^- \overset{K_5}{\rightleftharpoons} {Br_5}^- \qquad K'_5 = \frac{[Br_5^-]/c^\circ}{[Br_2]^2[Br^-]/c^{\circ 3}}$$

The only considered electrochemical reaction:

$$1/2\ Br_2 + e^- \rightleftharpoons Br^-$$

Assumed constant values [2]:

$$K'_3 = 16$$
$$K'_5 = 40$$

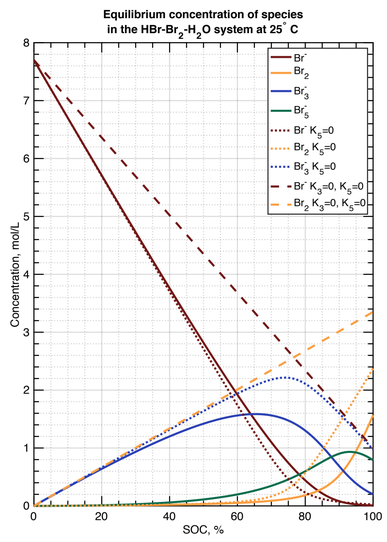
Define SOC (values prior to equilibrium):
0% SOC → 1M HBr, 3.35 Br_2
100% SOC → 7.7M HBr, 0.0M Br_2

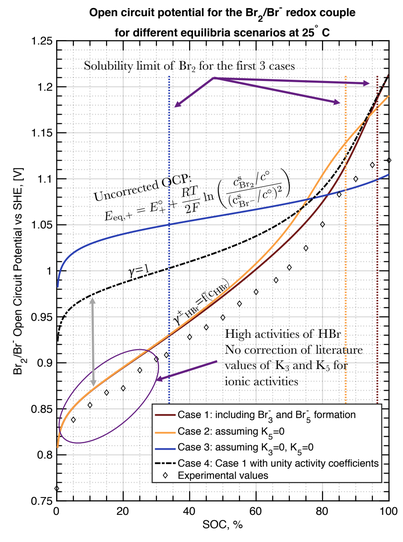
Br_2-containing species mass balance

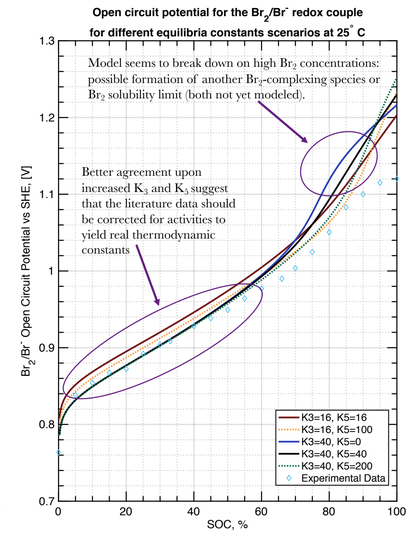
$$c_{Br_2} + c_{Br_3^-} + 2c_{Br_5^-} = c_B$$

Electroneutrality condition

$$c_{Br^-} + c_{Br_3^-} + c_{Br_5^-} = c_{H_3O+}$$







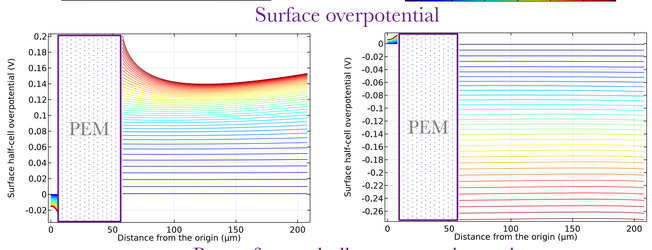
RESULTS

BASE CASE

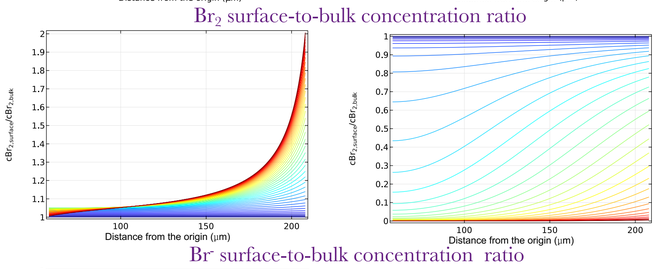
Charging

Discharging

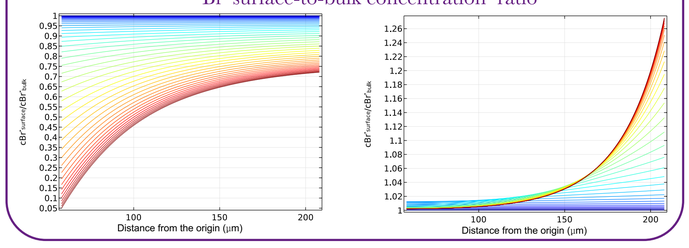
Surface overpotential



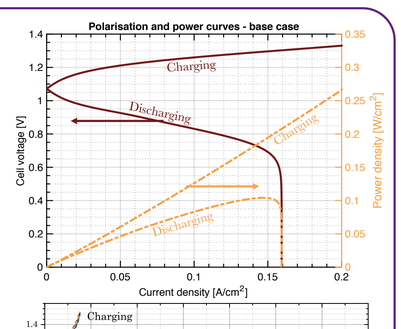
Br_2 surface-to-bulk concentration ratio



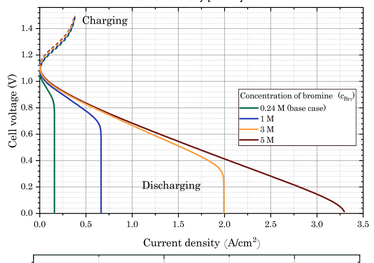
Br^- surface-to-bulk concentration ratio



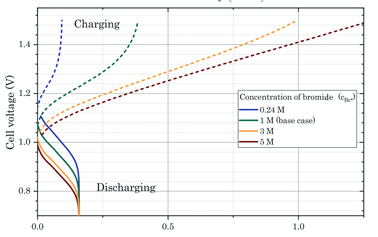
Base Case



Vary Br_2 concentration



Vary Br^- concentration



EXPECTED IMPACT & FUTURE WORK

- ✓ The implementation of computer modelling will conduce to accelerating the battery development process and optimization, and analysing the effect of cell design.
- ✓ By scrutinizing case studies performed by utilizing the 1D modelling approach, many conclusions about the cell performance can be drawn. The impact of critical engineering parameters such as electrolyte concentration, porosity, or temperature can be easily assessed and comprise a solid basis for further cell manufacturing process and commercialization by companies.
- ✓ Varying parameters in the 1D model produces physically meaningful responses. The model will be subjected to further validation using experimental methods obtained within the FlowCamp project.
- ✓ It was shown that polybromide complex formation and activity of ions in the solution have a tremendous impact on the open circuit potential of the H_2/Br_2 flow battery. A formation of higher polybromides is anticipated, given the discrepancy of modelling results with respect to experimental data at high states of charge (high Br_2 concentrations). The phenomenon will be addressed in the future work together with experimental validation and computational estimations of activity coefficients. Results from this study will be incorporated in further modelling approaches to reflect the thermodynamics and chemistry of the bromine/bromide half-cell more accurately.
- ✓ 1D model will be consecutively extended by adding advanced formulation of membrane transport processes to reflect the bromine crossover phenomenon which is critical in real cells and stacks and which impedes the development process. Understanding the bromine transport through an ionomer is indispensable for the efforts to reduce the total bromine flux through the separator.
- ✓ In order to asses another crucial issue - the flow distribution in half-cells, the model will also be implemented in 2D and 3D, with a coupling between Navier-Stokes or porous media fluid flow formulation and transport phenomena.

References

[1] Savinell, R. F. F. (1986). Theoretical and Experimental Flow Cell Studies of a Hydrogen-Bromine Fuel Cell, Part 1. M.S. Thesis. Final Report. Retrieved from https://ntrs.nasa.gov/search.jsp?R=19860019937

[2] Ramette, R. W., & Palmer, D. A. (1986). Thermodynamics of tri- and pentabromide anions in aqueous solution. *Journal of Solution Chemistry*, *15*(5), 387–395. https://doi.org/10.1007/BF00646261

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